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Research Article

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Effect of Ultrasonication on Stability of Oil in Water Emulsions

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Abstract

Effect of ultrasonic waves on stability of oil in water system of light liquid paraffin oil (HLB = 12) as internal phase and tween20 (HLB = 16.7), span20 (HLB = 8.6) as emulsifying agents was studied. A comparison was made to determine the stability of emulsions prepared by mechanical agitation method and ultrasonication technique. Droplet size measurement method was used to determine the stability of emulsions. Physico-chemical parameters like concentration of emulsifying agent, volume fraction of dispersed phase, viscosity of continuous phase by adding glycerin to water were compared apart from the effect of emulsification time on stability of emulsions prepared with mechanical stirring and ultrasound. Ocular micrometer was used to determine the droplet size of the dispersed phase.

Emulsions prepared by ultrasonic technique were found to be more stable for longer duration of time when compared to emulsions prepared by mechanical agitation which can be attributed to the small droplet size which is thermodynamically stabilized.

Ultrasonic technique gave more stable emulsions than with mechanical agitation method. Emulsification time, volume fraction of dispersed phase, viscosity of continuous phase and concentration of emulsifying agents played a major role in the stability of emulsions.

Keywords: Liquid paraffin, Tween 20, Span 20, emulsification, ultrasound technique, volume fraction of dispersed phase..

Introduction

In an emulsion system, the finely divided droplets are referred to as the dispersed phase, discontinuous or internal phase; the liquid surrounding the droplets is called the non-dispersed phase, continuous phase or external phase. The addition of a third component acting at the interface to retard phase separation is called emulsifier or emulsifying agent.

Since emulsions, in most instances, are two-phase systems, it is customary to define the type of emulsion by considering whether the oil is in the internal or external phase. If the oil is in the internal phase, the emulsion type will be an oil-in-water, o/w; or, conversely, if the water is in the internal phase, water-in-oil, w/o; type is achieved. Secondary emulsion (multiple-emulsion): it contains two internal phase, for instance, o/w/o or w/o/w. It can be used to delay release or to increase the stability of the active compounds.

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The first objective to be attained in emulsification is to reduce the internal phase (oil or water) into small globules [3-6]. This can be accomplished only if an external source of energy in the form of work is supplied. The energy may be in the form of human or mechanical work. Theoretically, it is possible to calculate the energy required to produce a quantity of an emulsion having a definite particle size by the use of the equation [7].

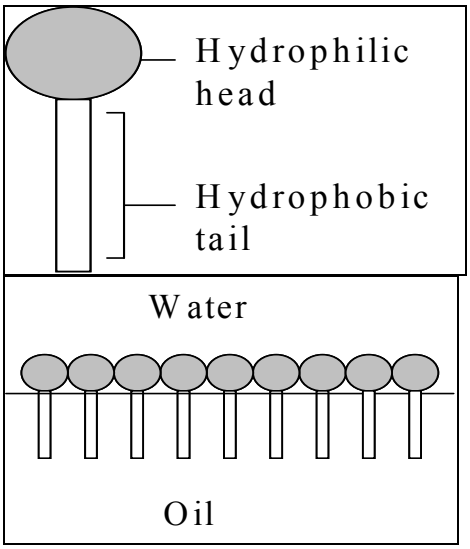
$$W = \gamma_{o/\omega} \cdot \triangle A$$

Surface free energy — Interfacial tension — Surface area

Where W is the free surface energy in ergs is, γ is the surface tension in dynes/cm, and ΔA, the surface area in cm^2. The work necessary to produce an emulsion of a specific volume and particle size may be reduced if the internal tension (γ) is lowered [8-9]. This may be accomplished by the addition of an emulsifying agent having surface-active properties. The selection of an emulsifying agent, which lowers the interfacial tension considerably, will be an important factor to consider when emulsification is desired [10-12]. However, it is not necessarily true that those agents who are not markedly reducing the interfacial tension are poor emulsifying agents [13].

Surface orientation

At the interface of oil and water, the molecule must posses a polar group and a nonpolar group, both of about equal magnitude. In this particular case, the molecule would orient itself in such a way that the polar group (hydrophilic head) will face the water, while the nonpolar group (hydrophilic tail) faces the oil [14-19]. Consider now the case of a molecule having a very large polar group in comparison to the non-polar group. This type of molecule will be more soluble in the water and, thus, will move away from the oil and enter the main portion of the water. The molecule with a large nonpolar group will migrate into the main portion of the oil phase [20].



Experience has shown that emulsifying agent having a greater degree of hydrophilic property than hydrophobic will usually produce an oil in water emulsion, while a more hydrophilic surface-active agent will usually give water in oil emulsion [20-23]. **Bancroft** noted this tendency a number of years ago and concluded that the phase in which the emulsifying agent was more soluble would be the continuous or the external phase [24-25].

Materials and methods

Light liquid paraffin oil (Sd Fine-chem. ltd), Tween 20 (polyoxyethylene sorbitan mono oleate), Span 20 (Sorbitan monooleate), Glycerin, distilled water, ocular microscope with stage micrometer.

Preparation of Emulsions

By mechanical agitation method

An emulsion of 60ml was prepared by taking, 20% of light liquid paraffin oil and span20 in a beaker and tween20 was added to 77% of distilled water in another beaker as tween20 is miscible in water and span20 is oil miscible followed by pouring dispersed phase to

continuous phase. Here percentage of emulsifying agent was kept to 3%. This composite solution was then subjected to mechanical agitation by placing the agitator at the middle of interface between the dispersed phase and continuous phase, at 1000 RPM. Proper mixing of the phases gives the good emulsion which is white in color.

By Ultrasonication method

Emulsion with above concentrations was prepared by applying the ultrasound using sonicator with adjustable height hadle with operating frequency of 20 KHz at 3mm of depth from the surface of the emulsion solution. Time of insonation is variable, which was measured by using stopwatch. Temperature of the sample was measured with thermometer, as time of insonation increases the temperature of the emulsion will increases. Emulsion prepared from ultrasonicator is milky white in colour.

Evaluation of emulsions

In this experiment, a study was made to compare the stability of emulsion prepared by two different methods i.e. mechanical stirring and ultrasonic horn tip method by examining the following physicochemical parameters affecting the emulsion stability.

1. Effect of stirring time and irradiation time.
2. Effect of volume fraction emulsifying agent.
3. Effect of volume fraction of oil phase or dispersed phase.
4. Effect of viscosity of continuous phase.

Effect of stirring time and irradiation time

Effect of time was studied on emulsions stability at fixed amount of emulsifying agent and fixed volume fraction of dispersed phase. Here 20% of dispersed phase volume and 3% of the emulsifying agent is used in total amount of 60ml oil. Volume fraction of dispersed phase $\varphi = 0.2$ and Volume of the dispersed phase is 12ml. Total amount emulsifying agent used is 3% means 1.8ml. in this volume fraction tween20 is 42% means 0.756ml and volume fraction span20 is 58% means 1.048ml. And continuous phase volume is 46.2ml.

Eight samples were taken and subjected to mechanical stirring at 1000rpm by varying the time from 1, 2, 3, 4, 5, 6, 7 and 8minutes. Similarly another eight samples of same compositional biphasic mixture were subjected to ultrasoincation by ultrasound horn tip, at 20 KHz frequency with increasing the time of insonation in the range of 1, 2, 3, 4, 5, 6, 7 and 8 minutes.

Immediately after completion of emulsification 1ml of emulsion sample was taken and diluted with 10ml of water in a test tube and was observed under microscopic stage micrometer to observe the number of droplets in the microscopic premises. By counting this number of droplets the average droplet size was measured by sauter diameter.

$$d_{32} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$$

Effect of volume fraction of emulsifying agent

Effect of volume fraction of the emulsifying agent was studied by keeping the time of emulsification (5min) and volume of the dispersed phase ($\varphi = 0.2$) as constant. The volume fraction of the emulsifying agent was varied from 3% to 15% and were subjected to emulsification by mechanical and ultrasonic method. Finally the droplet size of the emulsion was measured by stage micrometer as mentioned earlier.

Effect of volume fraction of oil phase or dispersed phase:

In this experiment emulsification time (5minutes) and volume fraction of emulsifying agent (9%) were kept constant with varying concentrations volume fraction of dispersed phase. In order to prevent the phase inversion, the total percentage of oil was not exceeded more than 40%. The prepared emulsions were subjected to emulsification by mechanical and ultrasonic method. Finally the droplet size of the emulsion

was measured by stage micrometer as mentioned above.

Effect of continuous phase viscosity

Viscosity of the solution was measured by using broke field viscometer. From the experiments considering the emulsification time, amount of emulsifying agent and volume fraction of the dispersed phase were kept constant, now by adding the glycerin to the water increased the viscosity of the continuous phase. In this process the volume fractional volume of emulsifying agent was 0.9 means 5.4ml, volume fraction of the dispersed phase is φ = 0.2 means 12ml, time of emulsification was 5minutes. To the remaining amount of 42.6ml of water, glycerin was added in the volume fraction 0.5, 1.0, 1.5 and 2.0 volume continuous phase. After the emulsions were prepared by mechanical agitation and ultrasonic method, the viscosity of the prepared emulsions was determined by viscometer followed by droplet size measurement using stage micrometer method as discussed earlier.

From the above experiments, a graph was plotted taking volume % of droplets and droplet size in microns with time of mechanical agitation or time of sonication applied to the sample.

Results and discussion

Effect of stirring time and irradiation time

By comparing the above figures (1 and 2) obtained for droplet size distribution of the droplets of emulsions, prepared from mechanical stirring, and ultrasonic irradiation, it can be observed that, as the emulsification time is increased the droplets distribution curve become narrow in shape, which indicates that number of droplets in uniform size in this narrow range are more and hence the stability of emulsion will be more. At minimum time of stirring or irradiation the droplet size distribution curve, become wider in range indicating droplets in this region are less in number, with wide spread of non uniform particles size distribution. As the time of emulsification was increased from 1min to 8min droplet distribution is in narrow range, increasing the stability of emulsions. As the time of sonication was increased temperature of the emulsion was found to increase which can be attributed to physical effect of ultrasonic irradiation.

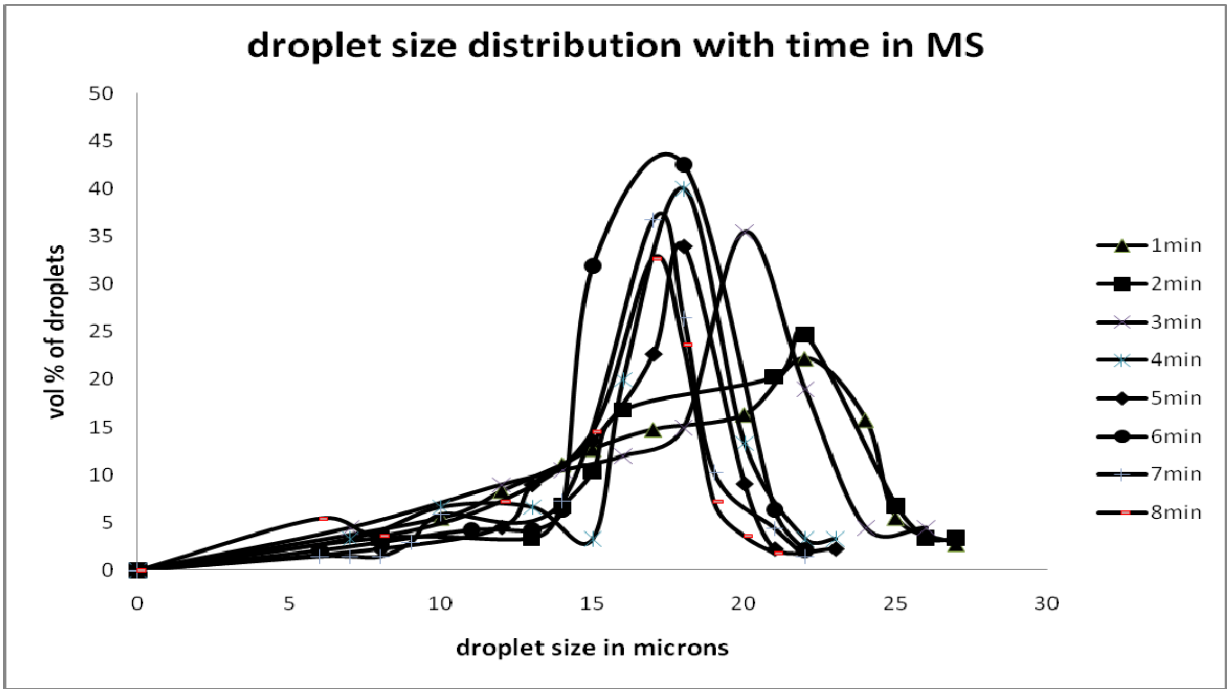


Figure 1: Volume of drop size distribution with emulsification time by mechanical stirring at constant emulsifying agent (3%) and volume fraction (φ = 0.2) of the oil.

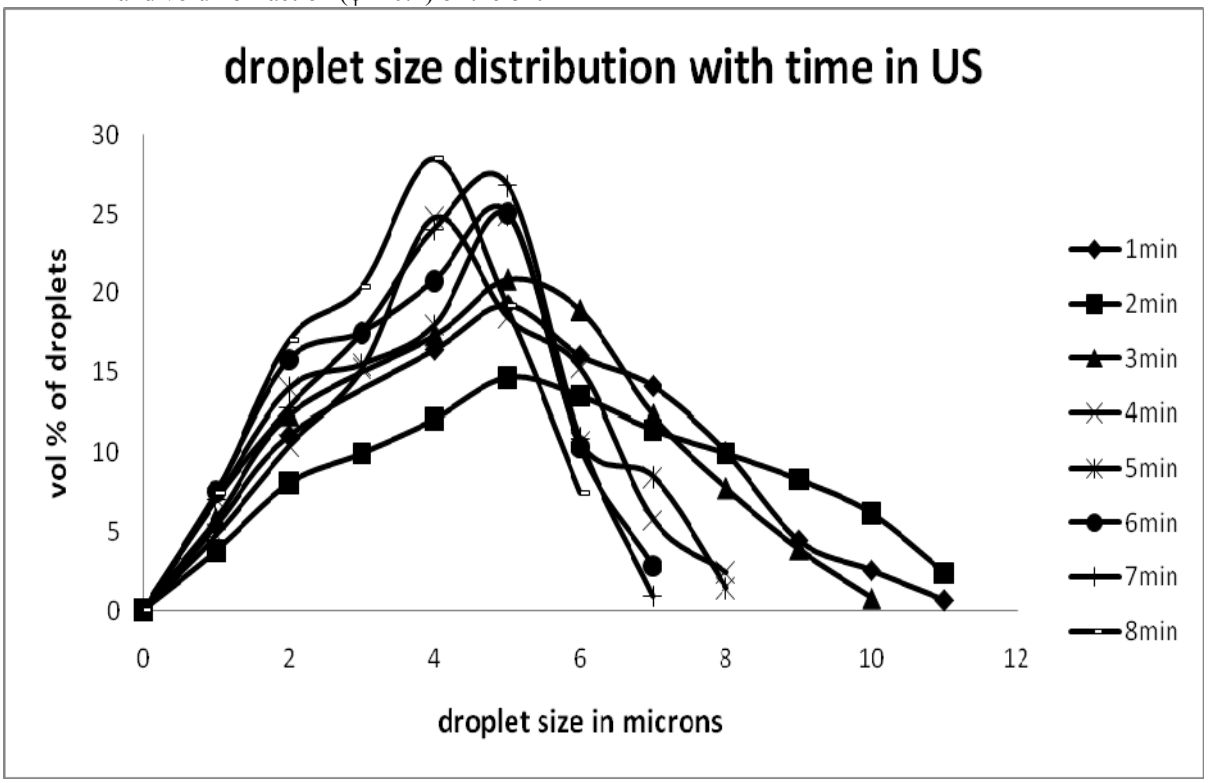


Figure 2: Volume of drop size distribution with emulsification time by ultrasonic irradiation at constant emulsifying agent (3%) and volume fraction (φ = 0.2) of the oil.

With an increase in the temperature, the interfacial tension as well as the viscosity is expected to decrease considerably. The decrease in the interfacial tension is observed to set in the interfacial instability, which increases the number of dispersed phase droplets. With an increase in temperature, the number of nuclei giving rise to cavitation may increase due to an increase in the vapour pressure of the cavitation medium. With an increase in the cavitational events and intensity, the breakage of large droplets to form small droplets is observed to be increasing. When the power is kept constant at 30 W, the droplets formed are initially small. They show a slight increase in size at a time of 1 min and then go on reducing if irradiated further until 8 min.

Effect of volume fraction of emulsifying agent

The surfactant plays a critical role in both droplet break-up and coalescence. The surfactant aids droplet break-up by lowering the interfacial tension, which reduces the resistance to droplet deformation. The most important role of the surfactant is to prevent the immediate re-coalescence of newly formed droplets by rapid adsorption to, and stabilization of, the newly formed interface.

Invariably the requirements of both droplet break-up and coalescence dictate that small molecule surfactants are the most suited to the formation of nano-emulsions because of their greater ability to rapidly adsorb to interface and their much lower dynamic interfacial tensions. As observed from the Figures (3 and 4), with the increase in the surfactant concentration from 3% to 9%, the particle size of the droplets was found to decrease up to 15% giving narrow particle size distribution. As the emulsifying agent amount increases it surrounds the oil droplets uniformly decreasing the interfacial tension between the oil droplets. With the increase in the emulsifying

agent concentration resulted in the formation of more stable emulsions with ultrasonicator than in the mechanical stirring.

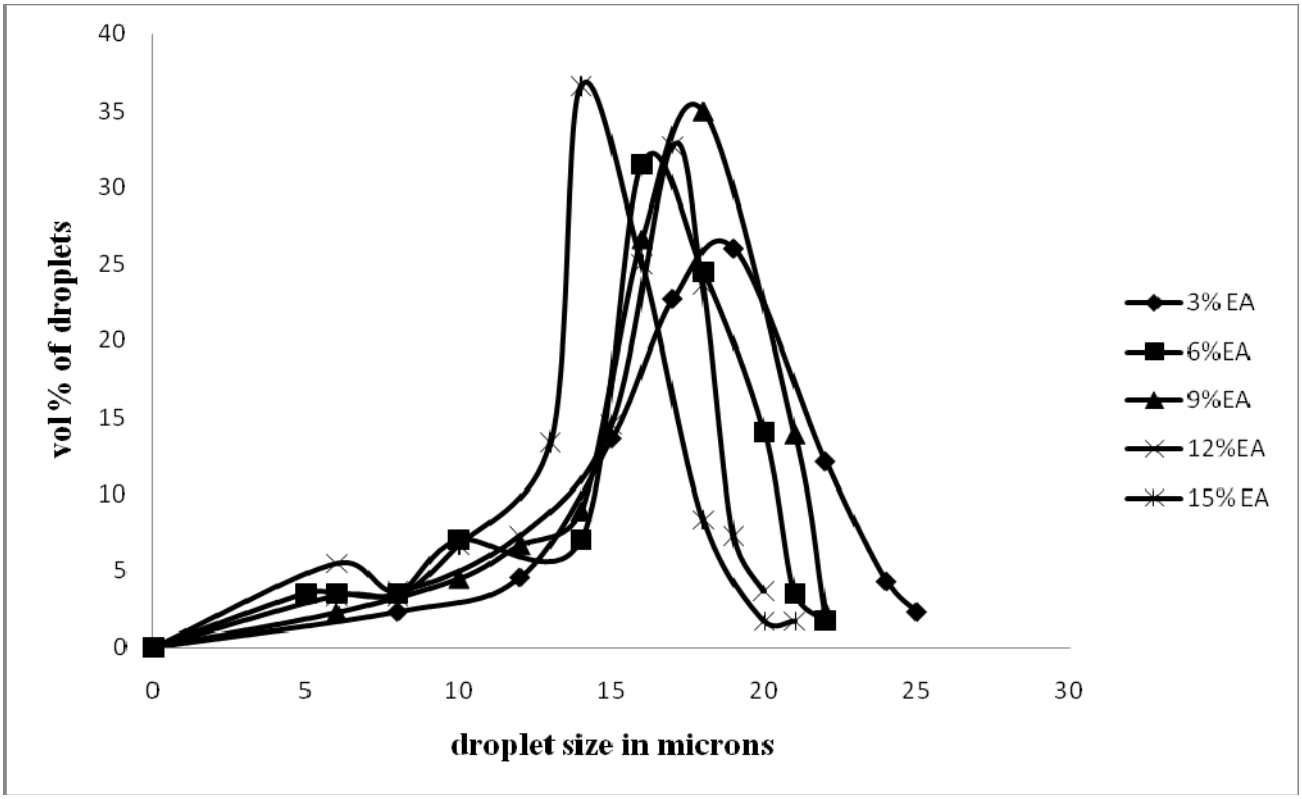


Figure 3: Effect of emulsifying agent on droplet size distribution of emulsions prepared from mechanical stirring.

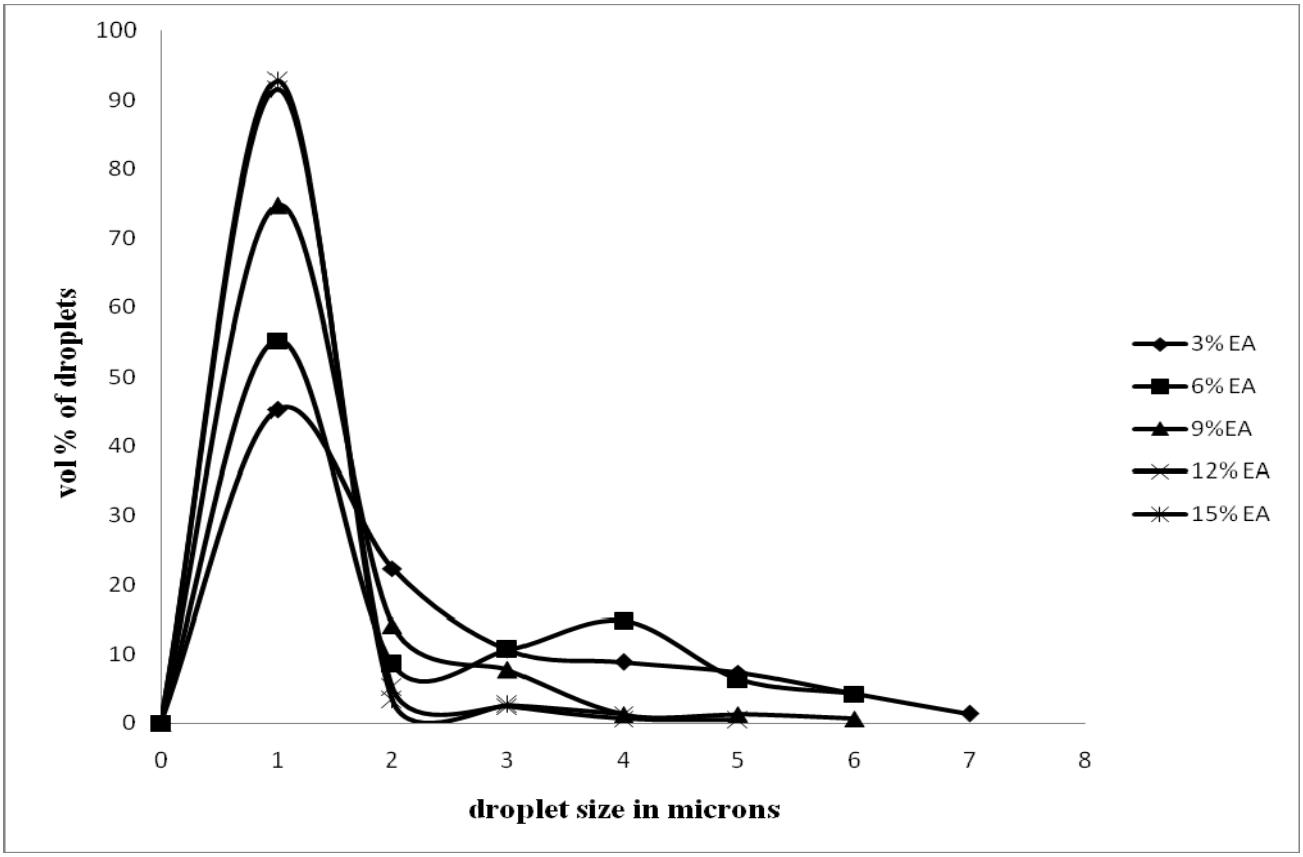


Figure 4: Effect of emulsifying agent on droplet size distribution of emulsions prepared from ultrasonication

Effect of volume fraction of oil phase or dispersed phase:

From Figures (5 and 6) it can be observed that with the increase in the volume fraction of the dispersed phase the droplet size of the oil phase was found to increase in both mechanical agitation and ultrasonication method. The droplet size of the oil phase in mechanical agitation varied from 13.9 to 25.1µm while in ultrasonication method it varied in the range of 1.29 to 4.21 µm. As the volume fraction of dispersed phase increases viscosity of dispersed phase increases then it is hard to break the oil droplets, and it is observed that droplet size is decrease in ultrasound than in the mechanical stirring because it requires more power to break the oil droplets and penetrate the droplets into the continuous phase. Mechanical stirring could not give required energy to break oil droplets. Using ultrasonic irradiation fragmentation of the droplets becomes more. However, at the starting of insonation it is hard to form a cavity bubble. This cavity bubble increases rapidly and collapse then the rupturing of the oil droplets becomes more. As the dispersed phase concentration increases, it requires more time to rupture the droplets. So size of the droplets increases by further addition of oil content. From the graphs, it can be observed that as the dispersed phase fraction increases droplet size distribution becomes wider with increase in mean number of droplets having non-uniform size. As the non uniformity of the droplets becomes more the stability of emulsion was found to decrease. Emulsions prepared from ultrasound were found to have narrow range of particles in the low fraction of dispersed phase. However, it becomes wider as the dispersion phase content increases.

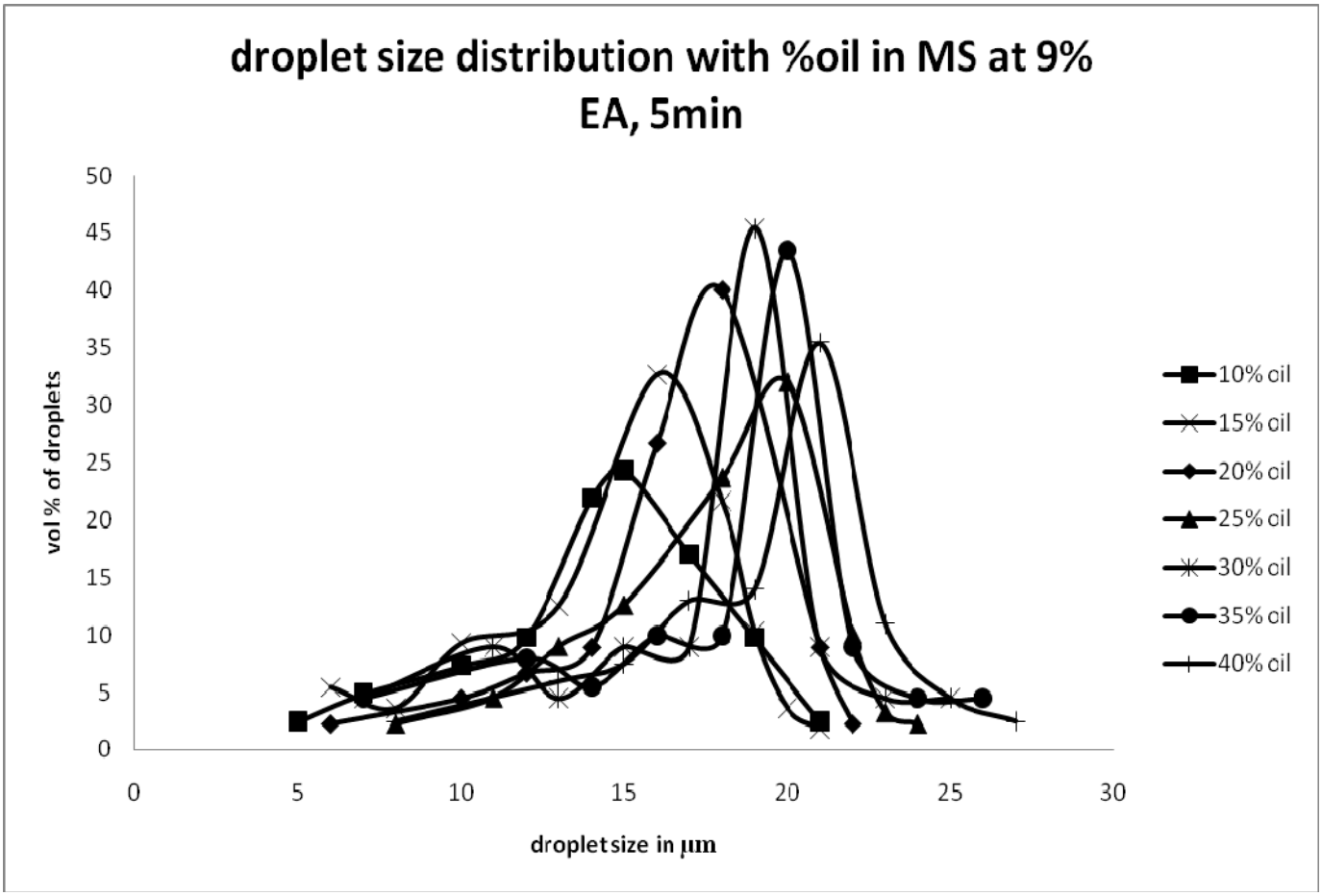


Figure 5: Droplet size distribution of the oil particles with varying concentrations of dispersed phase at constant emulsification time of 5minutes and emulsifying agent 9% in Mechanical agitation.

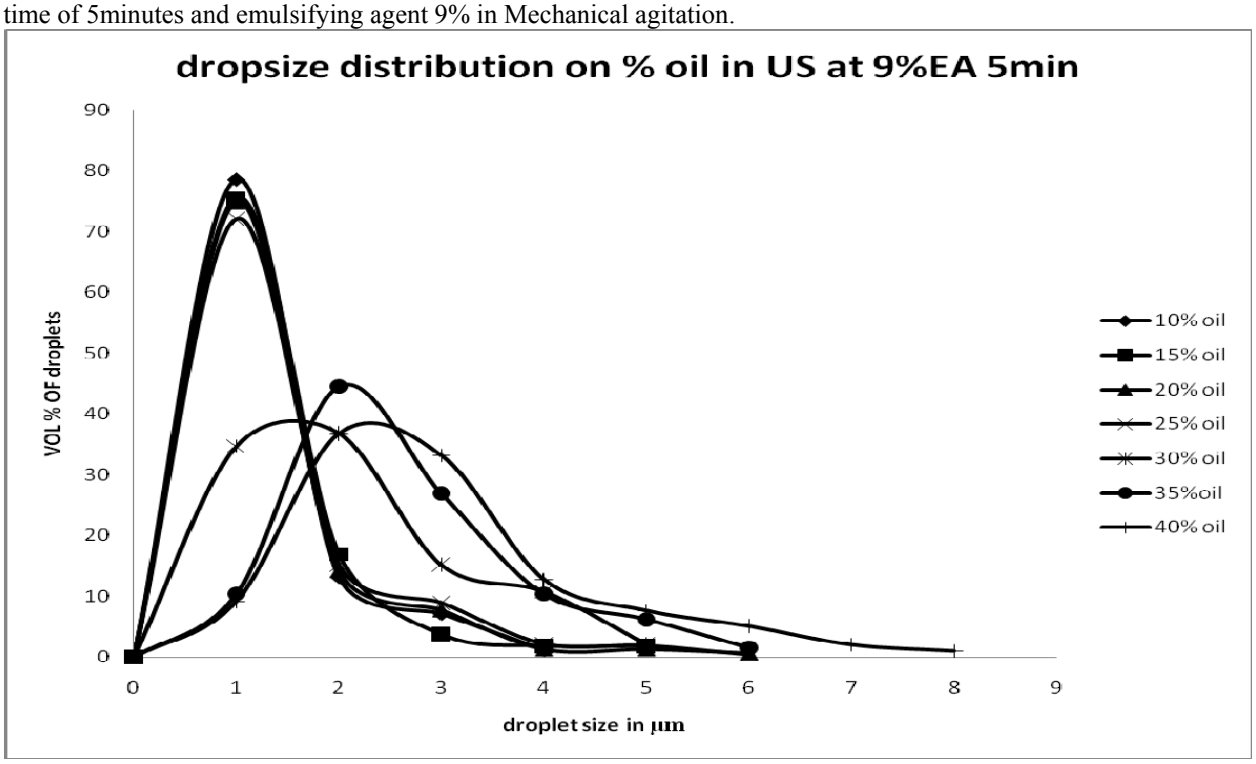


Figure 6: Droplet size distribution of the oil particles with varying concentrations of dispersed phase at constant emulsification time of 5minutes and emulsifying agent 9% in Ultrasonication

Effect of continuous phase viscosity

Here glycerin is act as secondary stabilizing agent, which was added to increases the viscosity of continuous phase thus reducing the mobility of droplets in order to prevent them from coalescing. As viscosity of the continuous phase increased stability of emulsion was found to increase which can be attributed to the continuous medium surrounding the droplets and it resist the coalescence of the droplets mean while there was increase in droplet size (Figure 7). Agglomeration of the droplets was found to decrease, but with the increase in the continuous phase viscosity it require more time of insonation or stirring to incorporate the oil phase into continuous phase. Droplet size also more as continuous phase viscosity increases.

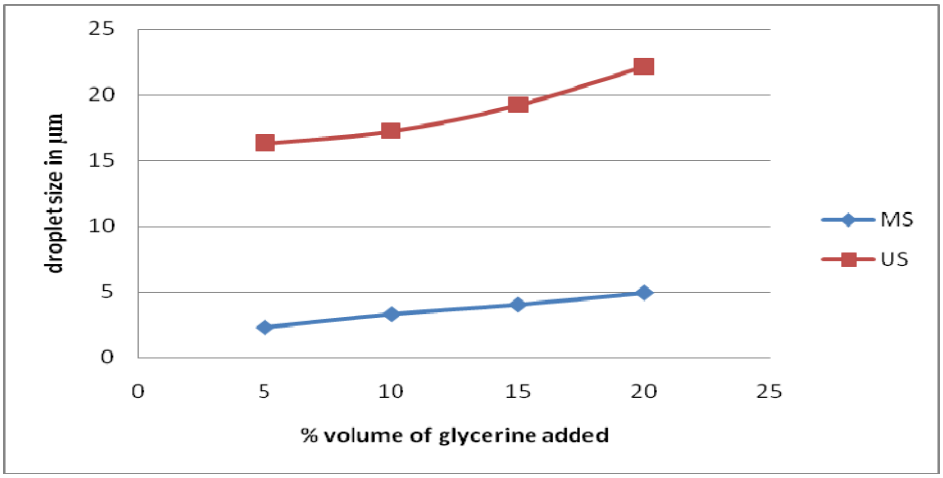


Figure 7; Droplet size of the oil with varying viscosity of continuous phase in mechanical agitation and ultrasonication technique.

Conclusion

With our simple, three-component, model system, comparison of two types of emulsification processes was made, first one using mechanical agitation method and the second one involving power ultrasound at low frequency (20 kHz), affords several interesting results in favor of the ultrasound technique. Smaller average drop sizes d32 (down to 1.125µm) can be obtained with ultrasound. Time of emulsification plays a major role in decreasing the droplet size of the emulsions. Ultrasound technique gives more stable emulsions than the mechanical stirring technique. Emulsifying agent resist the coalescence of droplets to agglomerate and brought the stable emulsions in both the mechanisms but in the ultrasound it effects more on stability as increased in volume fraction. Droplet size distribution of low content emulsifying agent emulsions is wider in range than with that are having more content of emulsifying agent. There is an increment in droplet size has been observed with increment in dispersed phase volume fraction but it was less in ultrasound technique when compared with mechanical stirring. Here droplet size increases as the viscosity of continuous phase increases but the stability increases with time of storage. An extension of this work would require the study on ultrasonic parameters like irradiation power irradiation frequency.

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